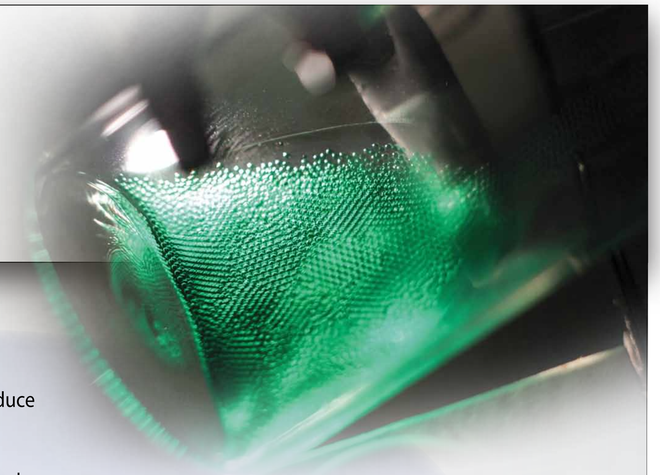
LLNL's robust catalysts and surface area enhancements dramatically speed solvent capture systems



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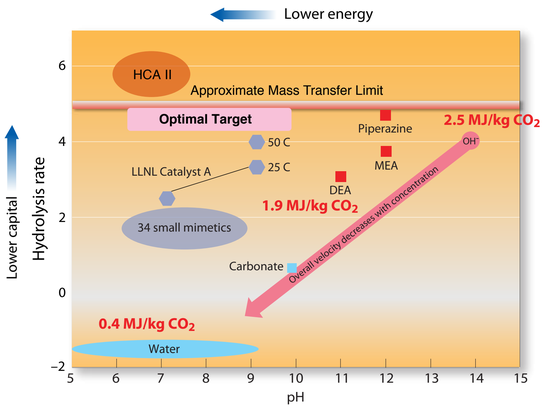
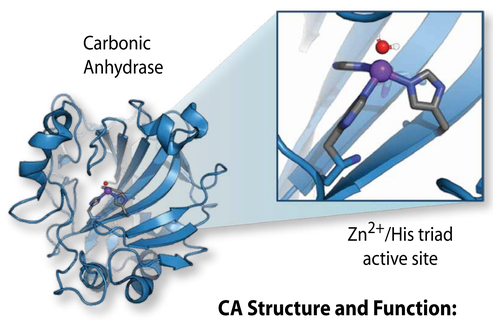
Introduction

- *Current carbon-capture technology*: high-pH solvents convert CO_2 to bicarbonate for separation
  - Problem: high energetic cost
- *Natural analogue*: enzyme carbonic anhydrase (CA) captures CO_2 at Zn^{2+} site at low pH
  - Problem: enzyme denatures in industrial applications
- *Solution*: Design improved catalysts that reproduce CA activity but remain robust in industrial applications
- These catalysts can provide fast kinetics even with solvents of lower pH and lower binding energy (see figure below), lowering overall system energy requirements.



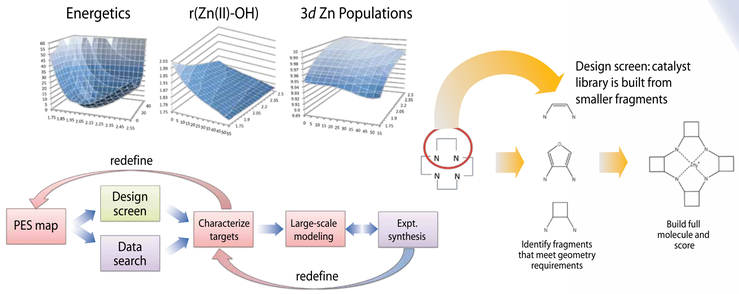


CA Structure and Function:

His triad, axial –OH, coordinate Zn^{2+} center, hydrophobic pocket collects CO_2
Mimics: optimize metal and ligand identity to improve kinetics;
later, try to include hydrophobicity to attract CO_2

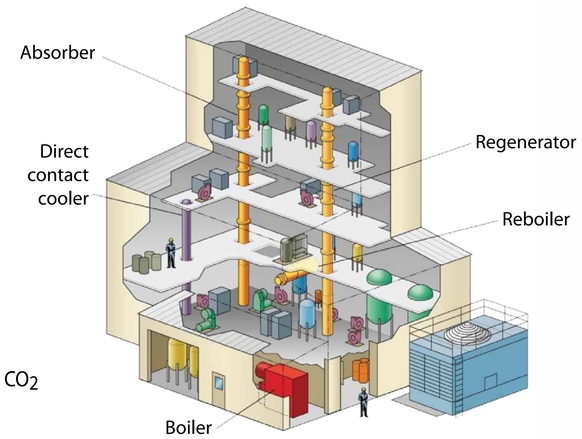
Catalyst Design

- *Method*: Plane-Wave Density Functional Theory (DFT)
- *Approach*: choose metal and ligand identity. Iterate over structural variables (distance, angles) with constrained relaxations, creating a Potential Energy Surface (PES) map (below left)
- *Individual maps* yield stability, electronic structure. Map comparisons yield trends in energetics with structures.
- *"Click chemistry"*: Search across design space using database of standard chemical fragments, trying all combinations. (below right)



Pilot-Scale Testing

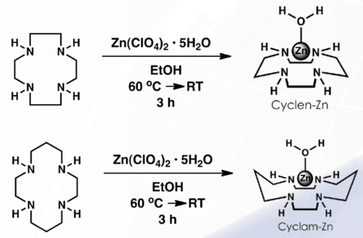
- Our industrial partner, Babcock & Wilcox, will test promising catalysts in their pilot-scale testing facility
- Their experience will provide feedback about real-world process conditions and assist in system design



Synthesis

- Computational search and characterization greatly reduce the number of compounds to be synthesized
- Mass spectroscopy and Nuclear Magnetic Resonance (NMR) used to verify structures of molecules synthesized
- Rates measured using stop-flow spectrometry

	LLNL Catalyst A	Post 18 hrs, 100˚C
pH 7.5	540	900
pH 9.0	2,500	2,260
50˚C	11,500	

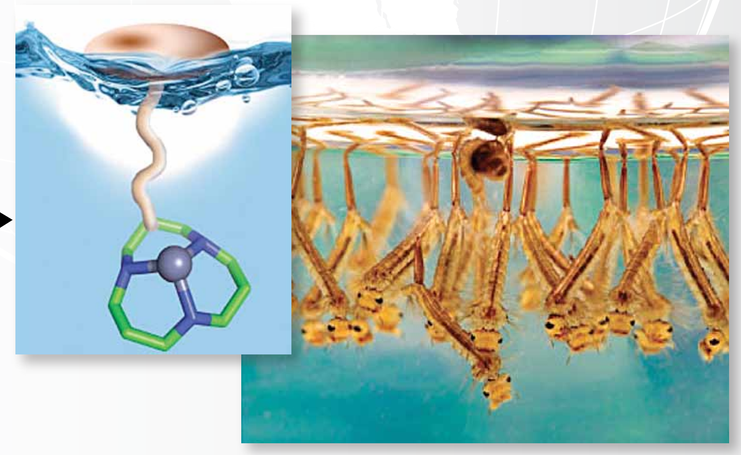


System Design

- Catalysts may require customized design for the overall capture process
- Faster kinetics from catalysts may allow for solvents of lower binding energy, lower-T regeneration, novel process configurations

Tethers

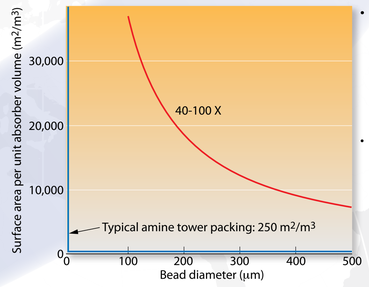
- Catalysts are only needed near the gas–liquid interface
- Solution: design catalyst to stay near the surface by attaching a long molecular chain with a hydrophobic group, shown here
- Initial calculations indicate that addition of long chain does not interfere with catalytic activity



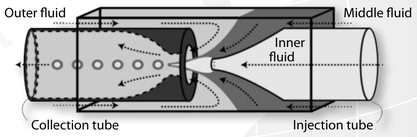
Encapsulation

- Microfabrication technology allows encapsulation of a solvent in a thin polymer shell (below)
- Target: 100-µm–diameter capsules with 5-µm wall thickness.
- Encapsulation creates large surface area

Surface area in bed of randomly-packed spherical beads is roughly 40-100x that in an amine tower (void space, ϵ = 0.38)



- Increased surface area roughly compensates for shell resistance at permeability of ~100 to 400 barrer (4000 to 40,000 on previous slide)
- Our minimum target shell permeability is 100 barrer



A.S. Utada, et al., *Science* **308**, 537 (2005)

Summary

This project uses an integrated, multi-disciplinary design process to tap the potential of biomimetic catalysts. These catalysts can enable a new class of energy-efficient and less-capital-intensive carbon-capture systems.

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